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(54) **Aqueous dispersions of urethane-acrylic copolymers and their use as finishing agents**

(57) The present invention relates to aqueous dispersions of urethane-acrylic copolymers containing fluorinated acrylic monomers, to their use as finishing

agents in oleo and water repellent treatment in the textile, leather and paper field and to a procedure for the preparation of said aqueous dispersions of polymers.

**EP 1 162 218 A1**

## Description

[0001] The present invention relates to aqueous dispersions of urethane-acrylic copolymers containing fluorinated acrylic monomers and to their use as finishing agents of textiles, leather and paper.

5 [0002] Particularly the invention relates to the use of said dispersions in oil-repellent and water-repellent treatments.

[0003] According to one of the main aspects the present invention a procedure for the preparation of said dispersions is described.

10 [0004] Aqueous emulsions containing fluorocarbonic resins are widely used as finishing agents in the textile, leather and paper fields, because they impart good characteristics of oil- and water repellency to the substrates treated there-with.

[0005] Many examples of aqueous emulsions containing fluorocarbonic resins, useful for the treatment of textiles, paper and leather, are described in literature.

15 [0006] By way of example, US 5164252 (US1) describes hydrophobizing and oleophobic compositions containing physical mixtures of a polymer containing perfluoroalkyl groups and of a cationically modified polyurethane dispersion, but it does not teach how to obtain a copolymer from said mixtures.

[0007] US 5346949 (US2) describes aqueous emulsions containing fluorinated and non-fluorinated monomers mixed with a water soluble non-urethane cationic polymer which is able to increase the fixing properties of the resin on textiles.

[0008] The water soluble cationic polymers used in US2 are expensive and commercially not easily available.

20 [0009] In US 5115013 (US3), the preparation and the use in the finishing of natural or synthetic materials of aqueous dispersions of polyurethane-acrylate containing from 5 to 30 percent of fluorine, are described; said dispersions are obtained by grafting a mixture of acrylic monomers (some of which containing fluorine) on not functionalized cationic polyurethane dispersions.

[0010] In EP 98752 (EP1) a process for the preparation of stable aqueous dispersions of oligourethane-acrylate vinyl terminated containing hydrophilic ionizable groups (anionic or cationic) is described.

25 [0011] In EP 183119 (EP2) copolymers of  $\alpha,\beta$ -ethylenically unsaturated monomers, modified with, from 5 to 60 percent by weight, extremes included, of an oligourethane containing ionizable groups and  $\alpha,\beta$  unsaturated terminal groups derived from acrylic and methacrylic monomers, are described

[0012] In EP2 neither the use of fluorinated monomers nor the use of said copolymers are cited in oil- and water repellent treatment.

30 [0013] EP2 also describes the process for the preparation of said compounds, process which is not suited for the synthesis of the cationic perfluorinated urethane-acrylate copolymers of the present invention, due to the poor emulsionability of the fluorinated monomers in the reaction medium.

[0014] According to the present invention, a group of fluorinated copolymers has been found, which is different in structure from the copolymers known for the same use and is prepared as a stable water dispersion.

35 [0015] Said water dispersion can be used as finishing agent in oil- and water-repellent treatment and is surprisingly effective even when used at low concentrations.

40 [0016] It is a main object of the present invention to provide aqueous dispersions of cationic urethane-acrylic copolymers containing fluorinated acrylic monomers obtained by radical polymerization in aqueous dispersion of fluorinated and non-fluorinated acrylic monomers (A) and of vinyl terminated polyurethane-acrylates containing cationic groups in aqueous dispersion (B).

[0017] It has been found that the product obtained from the reaction of A with B give excellent oil and water repellent effects to the materials treated and finished with it, effects that are surprisingly much better than the ones obtained using A and B in physical mixture.

45 [0018] Without giving an exhausting explanation of the reasons why the product obtained from the reaction of A with B exhibits a better performance in comparison with their physical mixtures, it is supposed that the fact that A and B are covalently bonded permits a better fixation of the active to textiles.

50 [0019] According to a fundamental aspect of the present invention, the amount of fluorinated acrylic monomer, which is the most expensive component of the mixtures normally used to obtain the expected effects, has been successfully decreased, while obtaining similar or better results in comparison with the ones obtained by the use of the separate components.

[0020] It is a further object of the present invention the procedure for obtaining said dispersions by radical polymerization of mixtures of fluorinated and non-fluorinated acrylic monomers, on vinyl terminated polyurethane-acrylates containing ionizable cationic groups.

55 [0021] It has now been found that the use of vinyl terminated urethane-acrylic copolymers as a base for the polymerization of fluorinated acrylic monomers permits a notable reduction of the amount of the surfactants that are normally used in polymerization or in the preparation of this kind of emulsions and that reduce the oil- and water repellent effects on textiles in the application step.

[0022] The vinyl terminated polyurethane-acrylates containing cationic groups in aqueous dispersion (B) can be

obtained following the procedure described in EP 98752.

[0023] According to EP 98752, aqueous dispersion of said vinyl terminated polyurethane-acrylates can be prepared by reacting, in a first step, an excess of an organic diisocyanate with a mixture of a diol containing ionizable groups and of an essentially linear macroglycol of the polyol-polyester type and/or polyol-polyether type having a molecular weight from 500 to 5,000 in order to obtain a prepolymer containing free isocyanate groups.

[0024] Said prepolymer is then converted into the vinyl terminated polyurethane-acrylate by reaction with a compound having hydroxyl groups able to react with isocyanic groups that has the following formula:



where R is a methyl group or a hydrogen atom and X is a hydroxyalkyl group.

[0025] The vinyl terminated polyurethane-acrylate is successively salified. The preparation of the vinyl terminated cationic polyurethane-acrylate and its successive salification can be done using the same molar ratios described in EP 98752.

[0026] The vinyl terminated polyurethane-acrylate thus obtained has a molecular weight from 2,000 to 50,000.

[0027] The utilizable organic diisocyanate of the present invention may be either of the aromatic, or of the aliphatic or of the cycloaliphatic type. Examples of suitable diisocyanate are 4,4'-dicyclohexylmethanediisocyanate, 1-isocyanate-3-isocyanate-methyl-3,5,5-trimethyl-cyclohexane (or isophorondiisocyanate), 2,2,4-trimethylhexamethylene diisocyanate in admixture with the 2,6,4-trimethylhexamethylene diisocyanate isomer, 2,4-toluenediisocyanate either alone or in admixture with the 2,6-toluenediisocyanate isomer, and 4,4'-diphenyl-methanediisocyanate, or mixtures thereof.

[0028] As ionizable diols, the diols bearing tertiary amine groups, such as methyldiethanolamine, are particularly suitable according to the present invention.

[0029] The utilizable macroglycols according to the present invention have a molecular weight from 500 to 5,000, preferably from 800 to 3,000, and are polyethers, polyesters or mixtures thereof.

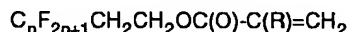
[0030] Examples of utilizable polyesters according to the present invention are polyesters prepared by polycondensation of preferably aliphatic acids or anhydrides, having from 4 to 9 carbon atoms with aliphatic diols having from 2 to 8 carbon atoms.

[0031] Examples of utilizable polyethers according to the present invention are the various types of polyethylene glycol, polypropylene glycol and, preferably, the polymerization products of tetrahydrofuran.

[0032] As compounds containing hydroxyl groups capable of reacting with the isocyanate groups particularly suitable according to the present invention are the following hydroxy-alkyl-acrylates or methacrylates: 2-hydroxyethyl-, 2-hydroxypropyl-, 3-hydroxypropyl- or 4-hydroxybutyl- acrylate or methacrylate, or mixture thereof.

[0033] In the present text with the expression "fluorinated and non-fluorinated acrylic monomers", we mean a mixture of from 40 to 70% by weight of fluorinated acrylic monomers and of from 30 to 60% by weight of non fluorinated acrylic monomers.

[0034] Fluorinated acrylic monomers utilizable according to the present invention have the following formula:



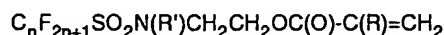
where

R is a methyl group or a hydrogen atom,

n is a number equal or smaller than 5, preferably from 5 to 12.

[0035] Preferably, the fluorinated acrylic monomers utilizable according to the present invention are ethyl acrylates or methacrylates substituted in the 2 position of the ethyl radical by a perfluoropentyl, perfluorooctyl or perfluorododecyl radical, or mixtures thereof.

[0036] For the realization of the present invention fluorinated monomers having the general formula



can also be used, where:

R and R' are an alkyl group or a hydrogen atom.

[0037] Examples of utilizable non-fluorinated acrylic monomers according to the present invention are: butadiene, isoprene, chloroprene, styrene,  $\alpha$ -methylstyrene, p-methylstyrene, vinylic halogenides (e.g. vinyl chloride, vinylidene

chloride, vinylidene fluoride, vinylic esters (e.g. vinyl acetate, vinyl propionate or vinyl stearate), esters of acrylic or methacrylic (e.g. methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate or methacrylate, decyl acrylate, lauryl acrylate or methacrylate, stearyl methacrylate, N,N-dimethylamino-ethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate or glycidyl methacrylate), acrylamide, methacrylamide, N-methylolacrylamide, acrylonitrile, methacrylonitrile, N-substituted maleic imides, or mixtures thereof.

[0038] The ratio between the mixture of fluorinated and non-fluorinated acrylic monomers (A) and the vinyl terminated polyurethane-acrylate containing cationic groups (B) is such that in the resulting copolymer the amount of (B) is from 5 to 50% by weight.

[0039] The polymerization in aqueous dispersion of fluorinated and non-fluorinated acrylic monomers onto vinyl terminated polyurethane-acrylate containing cationic groups cannot be carried out with the known techniques of emulsion polymerization, by warming up under traditional stirring, in the presence of surfactant and of initiator of polymerization generating free radicals, due to the fact that it is difficult to emulsify the perfluorinated monomers and that the contact between the acrylic monomers and the vinyl terminated polyurethane-acrylate cannot therefor assure the growth of the acrylic chain on the urethane-acrylate.

[0040] As a consequence, unstable emulsions are obtained by operating following the traditional method.

[0041] It has now been found that said polymerization can be carried out by previously preparing a pre-emulsion of the mixture of the fluorinated and non fluorinated acrylic monomers and of an aqueous dispersion containing the vinyl terminated polyurethane-acrylates.

[0042] In order to attain the aim of the present invention it is necessary to prepare stable pre-emulsions, by reducing the size of the particles to values lower than 0.15 micron, preferably lower than 0.10 micron. After having prepared the pre-emulsion it is possible to carry out the polymerization by warming up the pre-emulsion and by adding a solution, or an aqueous dispersion, of an initiator of radical polymerization into it, under stirring.

[0043] Useful initiators of radical polymerization are organic azoderivatives, organic hydroperoxides or peroxides, such as 2,2'-azobis-(2-methylpropionamidine) dihydrochloride, benzoyl peroxide, di-cumyl peroxide, tertbutyl-hydroperoxide, cumene hydroperoxide, p-menthane hydroperoxide, sodium, potassium or ammonium persulfate, used alone or together with a reducing agent such as sodium metabisulphite or sodium formaldehyde-sulfoxylate.

[0044] The amount of initiator employable ranges from 0.01 to 1% by weight, preferably from 0.01 to 0.2% by weight, referred to the total weight of the monomers.

[0045] The polymerization temperature may vary from 30° to 100°C, depending on the kind of initiator.

[0046] The preferred polymerization temperature range is from 40° to 70°C. The solution containing the polymerization initiator is normally added over a period of one or two hours, and anyway the reaction is carried on maintaining said temperature until the residual content of acrylic monomers does not exceed 0.1% by weight, referred to the initial amount of acrylic monomers.

[0047] Typically, the amount of urethane-acrylic copolymers in the aqueous dispersion useful for the realization of the present invention is from 20 to 30% by weight.

[0048] This range of concentrations is particularly appreciable by an industrial point of view as it permits to get sufficiently concentrated dispersions (avoiding the useless transportation of large quantities of water) and meanwhile it allows to obtain lower viscosities and an easier application.

[0049] In the most common form of realization of the present invention the reaction product of A and B is used in the form of an aqueous solution at a concentration of from 0.2 to 3% by weight in the composition used for finishing, preferably of from 0.5 to 2% by weight.

[0050] In the following examples all percentages are meant by weight.

#### Vinyl terminated polyurethane-acrylate dispersion preparation.

[0051] The vinyl terminated polyurethane-acrylate dispersion used in the following examples (here and hereafter named Polyurethane P) was prepared as follows.

[0052] Into a reactor equipped with stirrer, thermometer, reflux cooler, under nitrogen, 192.0 g of polytetrahydrofuran (PM 1,000), 20.0 g of methyl-diethanolamine and 0.046 g of benzoyl chloride are charged; then, under stirring, 45.4 g of hexamethylene diisocyanate and 70.7 g of 4,4'-dicyclohexyl-methane diisocyanate are added.

[0053] The reaction mixture is set at 90°C and this temperature is maintained until the -NCO content reaches 2.5%. After cooling down to 75°C the atmosphere was changed from nitrogen to air and 16.9 g of N-methylpyrrolidone and 9.4 g of hydroxypropyl acrylate are added. After 2 hours the prepolymer is diluted with acetone. At 50°C, 23.1 g of a 70% aqueous solution of methanesulfonic acid is added, taking care to maintain the temperature below 60°C, then 665.4 g of demineralized water are added under vigorous stirring. Acetone is then removed by vacuum distillation to obtain a translucent dispersion with a solid content of 30%.

Preparation of Solution 2.

[0054] For the application tests, an aqueous solution is prepared by mixing 2.76 g of Polyurethane P, 9.24 g of the dispersion obtained as described in Example 2 and 188 g of water (Solution 2).

Example 1.

[0055] 120.0 g of Polyurethane P are mixed with 45.0 g of  $\beta$ -(perfluorooctyl)ethyl acrylate (Foralkyl® AC/8N - Elf Atochem), 20.8 g of a 48% aqueous solution of methylolacrylamide, 30.0 g of methylmethacrylate, 6.0 g of Rolquat® S/35, 2.0 g of polyoxyethylene (30) nonylphenol, 2.0 g of polyoxyethylene (4) nonylphenol, 30.0 g of dipropylene glycol monomethylether, 3.0 g of 1-dodecanthiol and 208.2 g of demineralized water.

[0056] The mixture thus obtained is intimately emulsified by an Ultraturrax-T50 (Janke e Kunkel - IKA Labortechnik) apparatus for 5 minutes at 10000 rpm to obtain a stable pre-emulsion with particles having a size of 0.08 micron.

[0057] The pre-emulsion thus obtained is transferred into a reactor equipped with an anchor stirrer, thermometer and reflux cooler. The temperature is set at 60°C and under nitrogen atmosphere during 2 hours a solution obtained by dissolving 1.0 g of 2,2'-azo-bis-(2-methylpropionamidine) dihydrochloride (97%) in 50.0 g of demineralized water is added dropwise.

[0058] A stable aqueous dispersion is thus obtained with a solid content of 25% and pH 4.8.

Preparation of Solution 3.

[0059] For the application tests, an aqueous solution of the thus obtained dispersion is prepared, by mixing 12 g of it with 188 g of water (Solution 3).

Example 2.

[0060] 45.0 g of  $\beta$ -(perfluorooctyl)ethyl acrylate (Foralkyl® AC/8N - Elf Atochem) are mixed with 20.83 g of a 48% aqueous solution of methylolacrylamide, 30.0 g of methylmethacrylate, 6.0 g of Rolquat® S/35, 2.0 g of polyoxyethylene (30) nonylphenol, 2.0 g of polyoxyethylene (4) nonylphenol, 30.0 g of dipropylene glycol monomethylether, 3.0 g of 1-dodecanthiol and 184.2 g of demineralized water.

[0061] The mixture thus obtained is intimately emulsified by an Ultraturrax-T50 (Janke e Kunkel - IKA Labortechnik) apparatus for 5 minutes at 10000 rpm to obtain a stable pre-emulsion with particles having a size of 0.08 micron.

[0062] The pre-emulsion thus obtained is transferred into a reactor equipped with an anchor stirrer, thermometer and reflux cooler.

[0063] The temperature is set at 60°C and under nitrogen atmosphere during 2 hours a solution obtained by dissolving 1.0 g of 2,2'-azo-bis-(2-methylpropionamidine) dihydrochloride (97%) in 50.0 g of demineralized water is added dropwise.

[0064] A stable aqueous dispersion is thus obtained with a solid content of 25% and pH 5.3.

Preparation of Solution 1.

[0065] For the application tests, an aqueous solution of the thus obtained aqueous dispersion is prepared, by mixing 12 g of it with 188 g of water (Solution 1).

Application Tests

[0066] Preparation of the samples:

The three solutions prepared as described above (Solution 1, Solution 2 and Solution 3) are used.

The three solutions have a solid content of 1.5 % by weight and are used at such concentration on cotton, polyester, polyamide for foulard application, with pick-up values respectively of 70%, 50%, 50%.

The textile samples finished with each solution are then dried at 120°C for 1 minute and then heated at 160°C for 1 minute. After a 3 hours room climatization the following tests are performed:

## 1) Water repellency test.

[0067] The textile samples are tested in accordance with the AATCC-22 (Spray Test) Test Method.

[0068] 250 ml of demineralized water are poured on the textile sample.

[0069] The water repellency values are evaluated according to the following values

100	Dry surface
90	The surface is wetted by some drops
80	The surface is wetted by many drops
70	The surface is partially wetted
50	The surface is completely wetted
0	Water penetrates the sample

2) Oil repellency.

[0070] The textile samples are tested and evaluated according to values from 1 to 6, by using the following substances, according to AATCC-118 test method:

1	Nujol
2	65:35 - Nujol:n-hexadecane
3	n-hexadecane
4	n-tetradecane
5	n-dodecane
6	n-decane

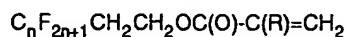
[0071] The water and oil repellency values obtained in the application tests carried out according to AATCC-22 e AATCC-118 test methods on textile samples finished with the three Solution 1, 2 and 3 are reported in Table 1.

Table 1.

	Solution 1		Solution 2		Solution 3	
	AATCC2 2	AATCC1 18	AATCC2 2	AATCC1 18	AATCC2 2	AATCC1 18
COTTON	50	4	70/80	5	90/100	6
POLYESTER	50/70	4	80	5	100	6
POLYAMIDE	90/100	4/5	90/100	5	100	6

#### Claims

1. Aqueous dispersions of cationic urethane-acrylic copolymers containing fluorinated acrylic monomers **characterized in that** said dispersions are obtained by radical polymerization in aqueous dispersion of fluorinated and non-fluorinated acrylic monomers (A) and of vinyl terminated polyurethane-acrylates containing cationic groups (B).
2. Aqueous dispersions according to claim 1. **characterized in that** said fluorinated and non-fluorinated acrylic monomers (A) consist of a mixture of from 40 to 70% by weight of fluorinated acrylic monomers and of from 30 to 60% by weight of non fluorinated acrylic monomers
3. Aqueous dispersions according to claim 2. **characterized in that** said fluorinated acrylic monomers have the following formula:

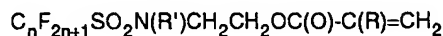


where

R is a methyl group or a hydrogen atom,  
n is a number equal or higher than 5.

4. Aqueous dispersions according to claim 3. **characterized in that** n is a number from 5 to 12.

5. Aqueous dispersions according to claim 2. **characterized in that** said fluorinated acrylic monomers have the following formula:



where:

R and R' are an alkyl group or a hydrogen atom.

6. Aqueous dispersions according to claim 1. **characterized in that** said vinyl terminated polyurethane-acrylates containing cationic groups (B) have a molecular weight from 2,000 to 50,000.

7. Aqueous dispersions according to claim 1. **Characterized by** the fact that they contain from 20 to 30% by weight of said cationic urethane-acrylic copolymers.

8. Process for the radical polymerization in aqueous dispersion of mixtures of fluorinated and non-fluorinated acrylic monomers (A) on vinyl terminated polyurethane-acrylates containing cationic groups (B), **characterized by** preparing a pre-emulsion of (A) and of an aqueous dispersion of (B) by reducing the size of their particles to a value <0.15 micron; by warming up said pre-emulsion to from 30° to 100°C and by polymerizing by adding an initiator of radical polymerization.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 01 11 2688

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IntCl.7)
A,D	US 5 164 252 A (MECKEL WALTER ET AL) 17 November 1992 (1992-11-17) * the whole document *	1	C08F290/06 C08F220/22 C09D151/08
A	US 5 623 016 A (KLEIN HEINZ-PETER ET AL) 22 April 1997 (1997-04-22) * column 7, line 41-45 *	1	
A	US 4 373 043 A (YAGI KAZUHISA ET AL) 8 February 1983 (1983-02-08) * column 8, line 3-22; claim 1 *	1	
P,X	DE 199 53 446 A (BASF COATINGS AG) 17 May 2001 (2001-05-17) * column 11, line 50-57 * * column 14, line 41-54 * * column 8, line 15-47 *	1	
			TECHNICAL FIELDS SEARCHED (IntCl.7)
			C08F C09D
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>2 August 2001</b>	Examiner <b>Meulemans, R</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 2688

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02-08-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5164252 A	17-11-1992	DE 3939341 A	06-06-1991
		DE 59005615 D	09-06-1994
		EP 0429983 A	05-06-1991
		JP 3172337 A	25-07-1991
US 5623016 A	22-04-1997	DE 4336206 A	27-04-1995
		AT 176678 T	15-02-1999
		AU 677427 B	24-04-1997
		AU 7599994 A	11-05-1995
		BR 9404213 A	04-07-1995
		CA 2134043 A	24-04-1995
		CZ 9402607 A	17-05-1995
		DE 59407799 D	25-03-1999
		DK 649865 T	20-09-1999
		EP 0649865 A	26-04-1995
		ES 2127329 T	16-04-1999
		FI 944925 A	24-04-1995
		HU 70882 A,B	28-11-1995
		JP 7233347 A	05-09-1995
		NO 944008 A	24-04-1995
		US 5571861 A	05-11-1996
US 4373043 A	08-02-1983	JP 1432647 C	24-03-1988
		JP 57139585 A	28-08-1982
		JP 62040468 B	28-08-1987
		DE 3129562 A	11-03-1982
		ES 504378 D	01-12-1982
		ES 8301251 A	16-02-1983
		FR 2487874 A	05-02-1982
		GB 2081724 A,B	24-02-1982
		IT 1137632 B	10-09-1986
DE 19953446 A	17-05-2001	WO 0134672 A	17-05-2001

EPO FORM P0418

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